Geometric Foundation of Thermo-Statistics, Phase Transitions, Second Law of Thermodynamics, but without Thermodynamic Limit*

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A *geometric* foundation thermo-statistics is presented with the *only axiomatic assumption of Boltzmann's principle* $S(E,N,V) = k \ln W$. This relates the entropy to the geometric area $e^{S(E,N,V)/k}$ of the manifold of constant energy in the (*finite-N*)-body phase space. From the principle, all thermodynamics and especially *all phenomena of phase transitions and critical phenomena can unambiguously be identified for even small systems.* The topology of the curvature matrix $C(E,N)$ of $S(E,N)$ determines regions of pure phases, regions of phase separation, and (multi-)critical points and lines. Phase transitions are linked to convex (upwards bending) intruders of $S(E,N)$, where the canonical ensemble defined by the Laplace transform to the intensive variables becomes multi-modal, non-local, (it mixes widely different conserved quantities). Here the one-to-one mapping of the Legendre transform gets lost. Within Boltzmann's principle, Statistical Mechanics becomes a *geometric theory* addressing the whole ensemble or the manifold of *all* points in phase space which are consistent with the few macroscopic conserved control parameters. This interpretation leads to a straight derivation of irreversibility and the Second Law of Thermodynamics out of the time-reversible, microscopic, mechanical dynamics. It is the whole ensemble that spreads irreversibly over the accessible phase space not the single N-body trajectory. This is all possible without invoking the thermodynamic limit, extensivity, or concavity of $S(E,N,V)$. Without the thermodynamic limit or at phase-transitions, the systems are usually not self-averaging, i.e. do not have a single peaked distribution in phase

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1

space. The main obstacle against the Second Law, the conservation of the phase-space volume due to Liouville is overcome by realizing that a macroscopic theory like Thermodynamics cannot distinguish a fractal distribution in phase space from its closure.

1   Introduction

There are many attempts to derive Statistical Mechanics from first principles. The earliest are by Boltzmann [1, 2, 3, 4], Gibbs [5, 6], and Einstein [7, 8, 9, 10]. The two central issues of Statistical Mechanics according to the deep and illuminating article by Lebowitz [11] are to explain how irreversibility (the Second Law of Thermodynamics) arises from fully reversible, microscopic dynamics, and the other astonishing phenomenon of Statistical Mechanics: the occurrence of phase transitions.

In this paper I want to present an easy, straightforward derivation of both aspects directly out of the microscopic time-reversal invariant Newton-mechanics invoking a minimum of assumptions. We will see how both problems are connected.There is an important aspect of Statistical Mechanics which to my opinion was not sufficiently considered up to now: Statistical Mechanics and also Thermodynamics are *macroscopic* theories describing the *average* * behavior of *all* N-body systems with the *same macroscopic constraints*. It is this fact and nothing else that leads in a simple and straightforward manner to the desired understanding of irreversibility, the Second Law for *finite N*-body systems, which obey a completely time reversible Hamiltonian dynamics, and leads simultaneously to the full spectrum of phase-transition phenomena. It is certainly essential to deduce irreversibility from reversible (here Newtonian) and not from dissipative dynamics as is often done because just the *derivation of irreversibility* from fully *reversible* dynamics is the main mystery of Statistical Mechanics. Here a first hint: Whereas a single trajectory in the (finite-N)-body phase space returns after a *finite* Poincaré recurrence time, a manifold of points develops in general irreversibly with time, see below. This taken alone would not yet allow for a rise of entropy. Since the entropy is the geometric measure of the ensemble (see below) the Second Law seems to be in conflict with Liouville's theorem which teaches us the invariance of the phase-space volume. This contradiction is solved in section 4.2 by defining a "measure" of the phase-space volume which is more adequate to the redundant nature of a macroscopic theory like Thermodynamics.

2   Minimum-bias deduction of Statistical Mechanics

Thermodynamics presents an economic but reduced description of a N-body system with a typical size of $N \sim 10^{23}$ particles in terms of a very few ($M \sim 3 - 8$) "macroscopic" degrees of

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*Here I do not speak of the *typical* behavior. This would only be the same if the system is *self-averaging*, which I do not demand, see below.

freedom (*dof*'s) as control parameters. Here I will allow also for much smaller systems of some 100 particles like nucleons in a nucleus. However, I assume that always $6N \gg M$. The belief that phase transitions and the Second Law can exist only in the thermodynamic limit will turn out to be false.

Evidently, determining only M *dof*'s leaves the overwhelming number $6N - M$ *dof*'s undetermined. *All* N-body systems with the same macroscopic constraints are *simultaneously* described by Thermodynamics. These systems define an *ensemble* $\mathcal{M}$ of points [†] in the N-body phase space. Thermodynamics can only describe the *average* behavior of this whole group of systems. I.e. it is a *statistical* or *probabilistic* theory. Considered on this level we call Thermodynamics thermo-statistics or since Gibbs *Statistical Mechanics*. The dynamics of the (eventually interacting) N-body system is ruled by its Hamiltonian $\hat{H}_N$. Let us in the following assume that our system is trapped in an inert rectangular box of volume V and there is no further conservation law than the total energy. The motion in time of all points of the ensemble follows trajectories in N-body phase space $\{q_i(t), p_i(t)\}|_{i=1}^N$ (I consider only classical mechanics) which will never leave the $(6N - 1)$-dimensional shell (or manifold) $\mathcal{E}$ of constant energy E in phase space. We call this manifold the *micro-canonical* ensemble. An important information which contains the whole equilibrium Statistical Mechanics including all phase transition phenomena is the *area* $W(E, N) =: e^{S/k}$ of this manifold $\mathcal{E}$ in the *n*-body phase space. Boltzmann has shown that $S(E, N, V)$ is the *entropy* of our system. Thus the entropy and with it equilibrium thermodynamics has a *geometric* interpretation.

Einstein called Boltzmann's definition of entropy as e.g. written on his famous epitaph

$$\boxed{\text{S=k·lnW}} \tag{1}$$

Boltzmann's principle [12] from which Boltzmann was able to deduce thermodynamics. Precisely W is the number of micro-states [‡] of the N-body system at given energy E in the spatial volume V and further-on I put Boltzmann's constant $k = 1$:

$$W(E, N, V) = tr[\epsilon_0 \delta(E - \hat{H}_N)] \tag{2}$$

$$tr[\delta(E - \hat{H}_N)] = \int_{\{q \in V\}} \frac{1}{N!} \left(\frac{d^3q\, d^3p}{(2\pi\hbar)^3} \right)^N \delta(E - \hat{H}_N), \tag{3}$$

ϵ_0 is a suitable energy constant to make W dimensionless, the N positions q are restricted to the volume V, whereas the momenta p are unrestricted. In what follows, I remain on the level of classical mechanics. The only reminders of the underlying quantum mechanics are

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[†] In this paper I denote ensembles or manifold in phase space by calligraphic letters like $\mathcal{M}$.

[‡] In the following I will call single points in the $6N$-dim phase-space *states* or micro-states which are specific microscopic realizations of the N-body system and correspond to single N-body quantum states in quantum mechanics. These must be distinguished from *macro-states* used in phenomenological thermodynamics c.f. section 4.1.

the measure of the phase space in units of $2\pi\hbar$ and the factor $1/N!$ which respects the indistinguishability of the particles (Gibbs paradox). With this definition, eq.(1), *the entropy $S(E,N,V)$ is an everywhere multiply differentiable, one-valued function of its arguments.* This is certainly not the least important difference to the conventional canonical definition. In contrast to Boltzmann [2, 3] who used the principle only for dilute gases and to Schrödinger [13], who thought equation (1) is useless otherwise, I take the principle as *the fundamental, generic definition of entropy.* In a recent book [14] cf. also [15, 16] I demonstrated that this definition of thermo-statistics works well especially also at higher densities and at phase transitions *without invoking the thermodynamic limit.* This is important: Elliot Lieb [17, 18] considers the additivity of $S(E)$ and Lebowitz [19, 11] the thermodynamic limit as essential for the deduction of thermo-statistics. However, neither is demanded if one starts from Boltzmann's principle. *Boltzmann's principle eq.(1) is the only axiomatic assumption necessary for thermo-statistics. This is all that Statistical Mechanics demands*, no further assumption must be invoked. Neither does one need extensivity [§], nor additivity, nor concavity of $S(E)$ c.f. [20].

In the next section I will show how in contrast to the common claim of textbooks Boltzmann's principle allows to define phase-transitions unambiguously in "Small" non-extensive systems as well as in normal "large" extensive systems where our more general definition of phase transitions (see below) will coincide with the conventional definition by the Yang-Lee singularities [21, 22]. Of course one should not wonder if some familiar gospels of conventional canonical thermo-statistics do not hold anymore in "Small" systems. This is discussed in some more detail in subsection 2.2

"Small" systems are either small many-body system like nuclei, atomic clusters etc. where surface effects are important or the largest systems possible like galaxies where the long-range gravity does not allow to extrapolate to the thermodynamic limit. Common to all "Small" systems is that they are inhomogeneous. I.e. the fundamental *homogeneity* assumption of conventional thermodynamics does not hold. Also at phase transitions of first order do the systems become inhomogeneous. *Interfaces are the characteristic signal of the transition.*

Thermodynamics describes the development of *macroscopic* features of many-body systems without specifying them microscopically in all details. Therefore, traditional thermo-statistics works in the thermodynamic limit of homogeneous infinitely large systems. Why then are we interested in "Small" systems? As will be explained later-on small systems reveal deep peculiarities of statistical mechanics much more sharply than macroscopic systems. Moreover, the overwhelming majority of systems in nature are "Small" systems, e.g. all astrophysical systems. The "thermodynamic limit" applies to some *ccm* but not to the really large ones.

[§]Dividing extensive systems into larger pieces, the total energy and entropy are equal to the sum of those of the pieces. I will call non-extensive systems where this is not the case in the following also "Small" systems [14] (with a capital S!) to stress the paradoxical point that the some of largest systems in nature (globular star clusters) belong to this group as well, nevertheless, they cannot be treated in the thermodynamic limit.

2.1 Why is the micro-canonical ensemble fundamental?

During the dynamical evolution of a many-body system interacting by short range forces the internal energy is conserved. Only perturbations by an external "container" can change the energy. I.e. the fluctuations of the energy are

$$\frac{\Delta E}{E} \propto V^{-1/3}, \tag{4}$$

and for large volumes these energy fluctuations may be ignored. If, however, the diameter of the system is of the order of the range of the force, i.e. the system is "Small" or non-extensive, details of the coupling to the container cannot be ignored.

2.2 (Non)-equivalence of ensembles and self-averaging

In contrast, the canonical ensemble does not care about these details, assumes the system is *homogeneous*, averages over a Boltzmann-Gibbs (exponential) distribution $P_{BG}\{q_\alpha, p_\alpha\} = \frac{1}{Z(\beta)} e^{-\beta \hat{H}\{q_\alpha, p_\alpha\}}$ of energy and fixes only the mean value of the energy by the temperature $1/\beta$. In order to agree with the micro, $e^{-\beta E} W(E)$ must be sharp in E i.e. self-averaging, which is usually not the case in non-extensive systems or at phase transitions of first order. Then one *must* work in the micro ensemble. The micro-ensemble assumes precise – perhaps idealized – boundary conditions for each particle independently of whether the system is small or large. Therefore, already Gibbs considered the micro-ensemble as the fundamental and the canonical as approximation to it. He demonstrates clearly the failure of the canonical in cases of phase separation or other situations where both ensembles differ, footnote on page 75 of [5], see also [23, 24].

There are important features where the micro-canonical statistics of "Small" systems deviates from the "canonical" structure of conventional thermo-statistics of extensive systems in the thermodynamical limit: E.g. *the familiar Legendre-transform structure, a paradigm of "canonical" thermo-statistics, is lost.* Clearly, without self-averaging, fixing an intensive parameter like the temperature T does not fix the energy sharply.

Most evident example is a transition of first order in the canonical ensemble at the transition temperature where the energy per particle fluctuates by the specific latent heat even in the thermodynamic limit. Related is the occurrence of *negative specific heat*, forbidden in the canonical thermodynamics, cf. section 3.2, found in recent experiments on nuclei [25, 26] which was predicted many years before [27]. Here, there are at least three energies for the same temperature c.f. section 3.3. The present discussions of non-extensive statistics as proposed by Tsallis [28] or recently by Vives et al. [29] clearly miss this crucial point. In the Tsallis statistics the entropy is expressed by the mean-values of the extensive quantities like $<E>$ [29, 30] controlled by a Lagrange parameter β or β^*, i.e. the Tsallis statistics works in the canonical

5

ensemble. Of course, this is equivalent to the micro-ensemble only if the variance of the energy is small. In one or the other way the thermodynamic limit and self-averaging is still demanded where Legendre transforms like $\beta \to E$ (may) become one to one. However, in the case of non-extensive systems the existence of the thermodynamic limit is unlikely and so is the uniqueness of the Legendre transformation.

3   Phase transitions within Boltzmann's principle

At phase-separation the system becomes *inhomogeneous* and splits into different regions with different structure. *This is the main generic effect of phase transitions of first order.* Evidently, phase transitions are foreign to the (grand-) canonical theory which assumes homogeneous density distributions. Consequently, in the conventional Yang-Lee theory, phase transitions [21] are indicated by the zeros of the grand-canonical partition sum where the grand-canonical formalism breaks down because of the Yang–Lee singularities of the grand-canonical potentials like $[\ln Z(T, \mu)]$. The micro-canonical formalism, esp. the micro-canonical entropy $S(E, N, V)$ remains *continuous and multiple differentiable* at phase transitions This is not the least important advantage of the micro-formalism.

In the following I show in sharp contrast to a statement by Schrödinger [13], Boltzmann's principle to be useful only for diluted gases, that Boltzmann's principle and the micro-canonical ensemble gives a much more detailed and more natural insight which moreover just corresponds to the experimental identification of phase transitions by interfaces (inhomogeneities).

3.1   Relation of the topology of $S(E, N, V)$ to the Yang-Lee zeros of $Z(T, \mu, V)$

Yang-Lee singularities define phase transitions in the thermodynamic limit. To explore the link, the grand-canonical partition sum may be obtained out of the micro-canonical one by a double Laplace transform. (In this limit it does not matter whether N is discrete or continuous.)

$$
\begin{aligned}
Z(T, \mu, V) &= \iint_0^\infty \frac{dE}{\epsilon_0} \, dN \, e^{-[E - \mu N - TS(E)]/T} \\
&= \frac{V^2}{\epsilon_0} \iint_0^\infty de \, dn \, e^{-V[e - \mu n - Ts(e,n)]/T} \\
&\approx \frac{V^2}{\epsilon_0} \iint_0^\infty de \, dn \, e^{-V[\text{const.}+\text{lin.}+\text{quadr.}]}
\end{aligned}
\tag{5}
$$

The double Laplace integral (5) can be evaluated asymptotically for large V by expanding the exponent as indicated in the third line to second order in $\Delta e, \Delta n$ around the "stationary point"

e_s, n_s where the linear terms vanish:

$$
\begin{aligned}
\frac{1}{T} &= \left. \frac{\partial s(e, n)}{\partial e} \right|_{stat.point} \\
\frac{\mu}{T} &= - \left. \frac{\partial s(e, n)}{\partial n} \right|_{stat.point}
\end{aligned}
\tag{6}
$$

the only terms remaining to be integrated are the quadratic ones.

If the eigen-curvatures, $\lambda_1 < 0, \lambda_2 < 0$, defined in eqn.(10), and eqns.(6) have a single solution (e_s, n_s), integral (5) is then a Gaussian integral and yields:

$$
\begin{aligned}
Z(T, \mu, V) &= \frac{V^2}{\epsilon_0} e^{-V[e_s - \mu n_s - Ts(e_s, n_s)]/T} \iint_{-\infty}^{\infty} dv_1 \, dv_2 \, e^{V[\lambda_1 v_1^2 + \lambda_2 v_2^2]/2} \tag{7} \\
&= e^{-(F(T, \mu, V) - \mu \bar{N})/T}. \tag{8}
\end{aligned}
$$

We now investigate the specific free energy in the thermodynamic limit $V \to \infty$:

$$
f(T, \mu, V) = \frac{F(T, \mu, V)}{V} \to e_s - Ts_s + \frac{T \ln\left(\sqrt{-\lambda_1}\sqrt{-\lambda_2}\right)}{V} + o(\frac{\ln V}{V}). \tag{9}
$$

Here $\boldsymbol{v_1}, \boldsymbol{v_2}$ are the eigenvectors in the $\{e, n\}$-plane and λ_1, λ_2 the eigenvalues of the curvature matrix with the determinant (Hessian):

$$
\det(e, n) = \left\| \begin{matrix} \frac{\partial^2 s}{\partial e^2} & \frac{\partial^2 s}{\partial n \partial e} \\ \frac{\partial^2 s}{\partial e \partial n} & \frac{\partial^2 s}{\partial n^2} \end{matrix} \right\| = \left\| \begin{matrix} s_{ee} & s_{en} \\ s_{ne} & s_{nn} \end{matrix} \right\| = \lambda_1 \lambda_2, \qquad \lambda_1 \geq \lambda_2 \tag{10}
$$

λ_1 can be positive or negative. If $\lambda_1 < 0$ and eqns.(6) have no other solution, the last two terms in eqn.(9) go to 0 in the thermodynamic limit ($V \to \infty$), and we obtain the familiar result for the free energy density:

$$
f(T, \mu, V \to \infty) = e_s - Ts_s. \tag{11}
$$

I.e. the *curvature λ_1 of the entropy surface $s(e, n, V)$ or the largest eigenvalue of the curvature matrix decides whether the grand-canonical ensemble agrees with the fundamental micro-ensemble in the thermodynamic limit.* If this is the case and eqns.(6) have a single solution or $s(e, n)$ touches its concave hull at e_s, n_s, then there is a pointwise one to one mapping of the micro-canonical entropy $s(e, n)$ to the grand-canonical partition sum $Z(T, \mu)$, and $\ln[Z(T, \mu)]/V$ or $f(T, \mu)$ is analytical in $z = e^{\beta \mu}$. Due to Yang and Lee we have then a single, stable phase [22]. Otherwise, *the Yang-Lee zeros of $Z(T, \mu)$ reflect anomalous points/regions of $\lambda_1 \geq 0$ {$\det(e, n) \leq 0$, in the cases studied here we have always $\lambda_2 < 0$]} where the canonical partition sum does not reflect local properties of the micro-ensemble, i.e. does not respect the conservation laws, and mixes conserved quantities.* This is crucial: As $\det(e_s, n_s)$ can be studied for finite or even small systems as well, this is the only proper extension of phase transitions to "Small" systems.

7

3.2 The physical origin of the wrong curvature

I will now discuss the physical origin of the convex (upwards bending) intruders in the entropy surface for systems with short-range coupling in two examples.

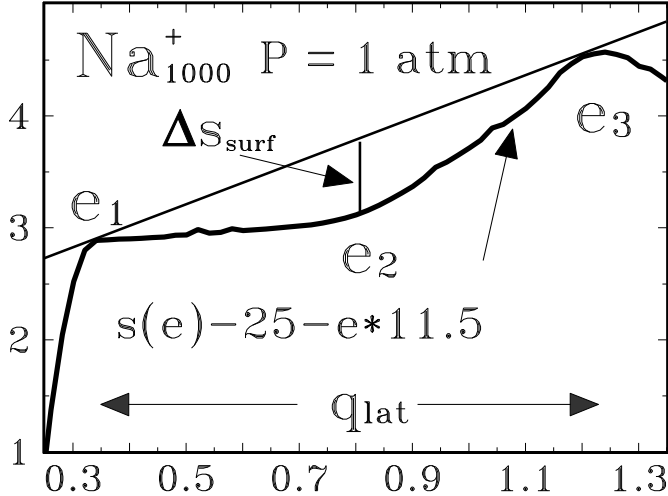### 3.2.1 Liquid-gas transition in sodium clusters

Figure 1: MMMC [14] simulation of the entropy $s(e)$ per atom (e in eV per atom) of a system of $N_0 = 1000$ sodium atoms with an external pressure of 1 atm. At the energy e_1 the system is in the pure liquid phase and at e_3 in the pure gas phase, of course with fluctuations. The latent heat per atom is $q_{lat} = e_3 - e_1$.

Attention: the curve $s(e)$ is artifically sheared by subtracting a linear function $25 + e * 11.5$ in order to make the convex intruder visible. $s(e)$ *is always a steeply monotonic rising function.* We clearly see the global concave (downwards bending) nature of $s(e)$ and its convex intruder. Its depth is the entropy loss due to the additional correlations by the interfaces. It scales $\propto N^{-1/3}$. From this one can calculate the surface tension per surface atom $\sigma_{surf}/T_{tr} = \Delta s_{surf} * N_0/N_{surf}$. The double tangent (Gibbs construction) is the concave hull of $s(e)$. Its derivative gives the Maxwell line in the caloric curve $T(e)$ at T_{tr}. In the thermodynamic limit the intruder would disappear and $s(e)$ would approach the double tangent from below. Nevertheless, the probability of configurations with phase-separations are suppressed by the (infinitesimal small) factor $e^{-N^{2/3}}$ relative to the pure phases and the distribution remains *strictly bimodal in the canonical ensemble.*

In the following table I compare the "liquid–gas" phase transition in sodium clusters of a few hundred atoms with that of the bulk at 1 atm. c.f. also fig.(1). In these calculations [31] we fixed the sampling volume for each energy at that value where

$$\left(\frac{\partial S(E,V)}{\partial V}\right) \bigg/ \left(\frac{\partial S(E,V)}{\partial E}\right) = 1 \text{ atm.} \tag{12}$$

8

(This is in sharp contrast to Andersen's "constant pressure ensemble" [32] where the volume can fluctuate at fixed energy). Conclusion: For systems with short range interactions a convex intruder in $s(e, n)$ appears with the fragmentation of the system into several clusters and monomers. The depth of the intruder (surface entropy) scales with the number of surface particles. I.e. the convex intruder signals the preference of the system to become inhomogeneous, which is the characteristic signal for the separation of different phases (liquid and gas) at a phase transition of first order.

	N_0	200	1000	3000	**bulk**
	$T_{tr}\ [K]$	940	990	1095	**1156**
	$q_{lat}\ [eV]$	0.82	0.91	0.94	**0.923**
Na	s_{boil}	10.1	10.7	9.9	**9.267**
	Δs_{surf}	0.55	0.56	0.44	
	N_{surf}	39.94	98.53	186.6	**∞**
	σ/T_{tr}	2.75	5.68	7.07	**7.41**

Table 1 : Parameters of the liquid–gas transition of small sodium clusters (MMMC-calculation) in comparison with the bulk for rising number N_0 of atoms, N_{surf} is the average number of surface atoms (estimated here as $\sum N_{cluster}^{2/3}$) of all clusters with $N_i \geq 2$ together. $\sigma/T_{tr} = \Delta s_{surf} * N_0/N_{surf}$ corresponds to the surface tension. Its bulk value is adjusted to agree with the experimental values of the a_s parameter which we used in the liquid-drop formula for the binding energies of small clusters, c.f. Brechignac et al. [14], and which are used in this calculation for the individual clusters.

3.2.2 The global phase diagram portrayed by the topology of the entropy surface $S(E, N)$, here for Potts lattice gases

Having discussed in the previous example a system with a single thermodynamic degree of freedom or control parameter (the energy E) we will now study more subtle features. If the system has two, or more, control parameters, e.g. energy $E = Ve$ and particle number $N = Vn$, where V is the volume, we can have phase boundaries and critical points. This reminds of the classical $P - V$ diagram of the liquid–gas phase transition in Van-der-Waals theory. We are now also able to identify multi-critical points. These were previously studied in the canonical ensemble only, where sophisticated finite size scaling is needed to identify these points. As example we investigate the 3-states diluted Potts model on a *finite* 2-dim (here $L^2 = 50^2$) lattice with periodic boundaries (to minimize effects of the external surfaces of the system). The model is defined by the Hamiltonian:

$$H = - \sum_{i,j \in n.n.pairs} o_i o_j \delta_{\sigma_i, \sigma_j} \tag{13}$$
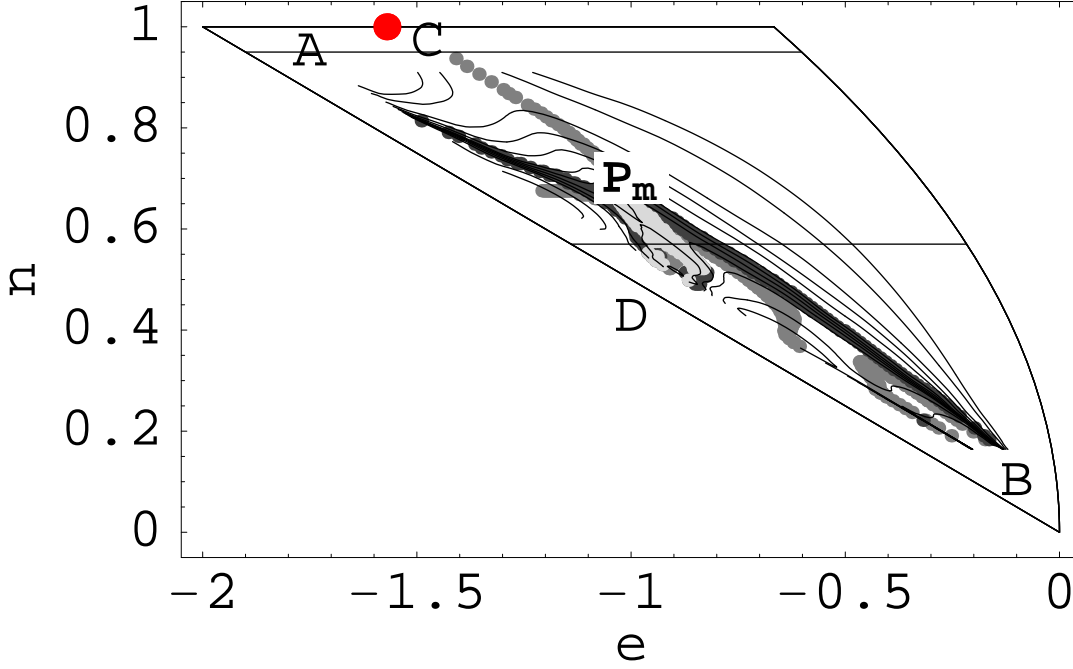
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$$n = L^{-2}N = L^{-2}\sum_i o_i.$$

Figure 2: Global phase diagram or conture plot of the curvature determinant, eqn.(10), of the 2-dim Potts-3 lattice gas with $50 * 50$ lattice points, n is the number of particles per lattice point, e is the total energy per lattice point; Dark grey lines: det $= 0$, boundary of the region of phase coexistence (det < 0) in the triangle AP_mB; Light grey lines: minimum of $\det(e,n)$ in the direction of the largest curvature ($\mathbf{v}_{\lambda_{max}} \cdot \nabla \det = 0$), lines of second order transition; In the triangle AP_mC pure ordered (solid) phase (det > 0); Above and right of the line CP_mB pure disordered (gas) phase (det > 0); The crossing P_m of the boundary lines is a multi-critical point. It is also the critical end-point of the region of phase separation (det < 0). The light gray region around the multi-critical point P_m corresponds to a flat (cylindric) region of $\det(e,n) \sim 0$ and $\nabla \lambda_1 \sim 0$, details see [15]; C is the analytically known position of the critical point which the ordinary $q = 3$ Potts model (without vacancies) would have *in the thermodynamic limit* $N \to \infty$.

Each lattice site i is either occupied by a particle with spin $\sigma_i = -1, 0$, or 1, or it is empty (vacancy). The sum is over pairs of neighboring lattice sites i, j, and the occupation numbers are:

$$o_i = \begin{cases} 1 & \text{, spin particle in site } i \\ 0 & \text{, vacancy in site } i \end{cases} . \tag{14}$$

This model is an extension of the ordinary $(q = 3)$-Potts model to allow also for vacancies. How to understand the line CP_m of second-order transition? At zero concentration of vacancies ($n = 1$), we know that the system has in the thermodynamic limit ($N \to \infty$) a continuous phase transition at $e_c = 1 + \frac{1}{\sqrt{q}} \approx 1.58$ [33, 34]. With rising number of vacancies the probability decreases to find a pair of particles at neighboring sites with the same spin orientation. I.e. this is analog to a larger number q_{eff} of spin orientation on each lattice site in the ordinary (completely filled) Potts model. We know that there the transition of second order becomes a transition of first order for $q > 4$. Similarly, the inclusion of vacancies has the effect of an increasing effective $q_{eff} \geq 3$. This results in an increase of the critical energy of the continuous phase transition with decreasing n and provides a line of continuous transition, which is supposed to terminate when q_{eff} becomes larger than 4. From here on the transition becomes first order. At smaller energies the system is in one of the three ordered phases (spins predominantly parallel in one of the three possible directions). Figure (2) shows clearly how for a small system of $50 * 50$ lattice points all phenomena of phase transitions can be studied from the topology of the determinant of curvatures (Hessian 10) in the micro-canonical ensemble. [In this example the second curvature is always $\lambda_2 < 0$ and consequently, sign(det) $= -$sign(λ_1)].

3.3 Conclusion and systematics of phase transitions in the micro-ensemble

Now we can give a systematic and generic classification of phase transitions in terms of the topology of curvatures of $s(e, n)$ which applies also to "Small" systems:

- A **single stable** phase by $\lambda_1 < 0$. Here $s(e, n)$ is locally concave (downwards bended) in both directions and eqns.(6) have a single solution e_s, n_s. Then there is a one to one mapping of the grand-canonical $\leftrightarrow$ the micro-ensemble. The order parameter is the direction $\boldsymbol{v}_1$ of the eigenvector of largest curvature λ_1. In many situations one may have only locally $\lambda_1 < 0$, but there may be further solutions to eqns.(6) farther away. Such cases have no equivalent in the canonical ensemble, here we will still speak of regions in $\{e, n\}$ of pure phases embedded in regions of phase-separation.
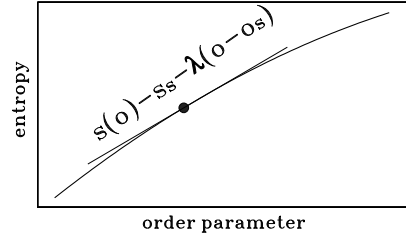
- A **transition of first order** with phase separation and surface tension (c.f.subsection 3.2.1) indicated by $\lambda_1 > 0$. $s(e, n)$ has a convex intruder (upwards bended) in the direction $\boldsymbol{v}_1$ of the largest curvature. Then eqns.(6) have multiple solutions, at least three. The system is in the pure liquid phase at o_1 and in the pure gas phase at o_3. The whole convex area of $\{e,n\}$ is mapped into a single point (T, μ) in the grand-canonical ensemble (non-locality). I.e. if the largest curvature of $S(E, N)$ is $\lambda_1 > 0$ *both ensembles are not equivalent, the (grand-) canonical ensemble is non-local in the order parameter and violates basic conservation laws.* C.f. [14, 15, 16, 35].
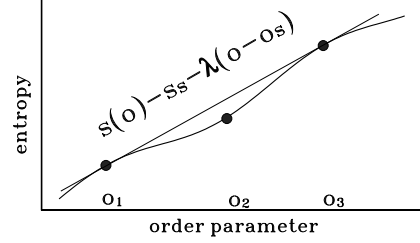
The region in the plane of conserved control-parameters e, n where we have a separation of different phases, where $\lambda_1(e, n) > 0$, is bounded by lines with $\lambda_1(e, n) = 0$. Here one of the two coexisting phases gets depleted. A special point on this boundary is the end-point of the transition of first order,

- where we have a **continuous ("second order")** transition with vanishing surface tension, where two neighboring phases become indistinguishable. This is at points where the two stationary points o_1, o_3 move into one another to become the critical end-point of the first order transition. This is then also a maximum of λ_1. I.e. where $\lambda_1(e, n) = 0$ and $\boldsymbol{v}_{\lambda_1=0} \cdot \boldsymbol{\nabla} \lambda_1 = 0$. These are the *catastrophes* of the Laplace transform $E \to T$. Here $\boldsymbol{v}_{\lambda_1=0}$ is the eigenvector of the curvature matrix belonging to the largest curvature eigenvalue $\lambda_1 = 0$. ($\boldsymbol{v}_1$ plays the role of the order parameter of the transition. In this direction one moves fastest from one phase to the other.) Furthermore, there may be also whole lines of second-order transitions like the line CP_m in figure (2) or e.g. in the anti-ferro-magnetic Ising model c.f.[14].

- Finally, there is further a **multi-critical point** P_m where more than two phases become indistinguishable. This is at the branching of several lines in the $\{e, n\}$-phase-diagram with $\lambda_1 = 0$, $\boldsymbol{\nabla} \lambda_1 = \boldsymbol{0}$. Fig. 2 gives an illustration of a multi-critical point in a small system.

4 Geometric foundation of irreversibility and the Second Law of Thermodynamics

In the next three sections I want to deduce irreversibility and the Second Law of statistical mechanics from the fundamental, microscopic, reversible Newton mechanics of the N-interacting-particle dynamics. I apologize this requires some more (very little) mathematics. However, I

believe this is still much simpler than any alternative derivation proposed so far.

After succeeding to deduce equilibrium statistics including all phenomena of phase transitions from Boltzmann's principle alone, even for "Small" systems, i.e. non-extensive many-body systems [14], it is challenging to explore how far this "most conservative and restrictive way to thermodynamics" [36] is able to describe also the *approach* of (possibly "Small") systems to equilibrium and the Second Law of Thermodynamics. Thermodynamics describes the development of *macroscopic* features of many-body systems without specifying them microscopically in all details.

Before going into details I want to state the Second Law of Thermodynamics in its perhaps most transparent way as follows, c.f. Gallavotti [37], page32: Entropy as defined by Boltzmann's principle (eq.1) of an *isolated many-body system approaching equilibrium either increases or remains constant.*

One of the most piercing arguments against Boltzmann's statistical explanation of the Second Law is due to Zermelo [38, 39]: A Hamiltonian system moves on a closed trajectory in its N-body phase-space and returns after a long recurrence time, the Poincaré recurrence time. So after some time entropy should decrease again. Boltzmann's answer was: As this time is astronomically large for a usual macroscopic systems ($\sim 10^{23}$ particles) these recurrences are irrelevant for practical life. However, for a small system with a few tens of particles this time becomes relevant and a reinvestigation of Zermelo's objection is necessary. Moreover, this question is also of fundamental importance: Is irreversibility and the Second Law only due to the extremely long recurrence times (Boltzmann) of macroscopic systems or are these a general property of the basic *probabilistic* nature of thermo-statistics? Existing proofs of irreversibility out of the microscopic time-reversible dynamics are using infinitely sized systems and thus put Zermelo's objection aside.

4.1 Measuring a macroscopic observable from a microscopic point of view

Before I address the Second Law, I have to clarify what I mean with the label "macroscopic observable". A single point $\{q_i(t), p_i(t)\}_{i=1,\cdots,N}$ [¶] in the N-body phase space corresponds to a detailed specification of the system with all degrees of freedom (dof's) completely fixed at time t, i.e. a microscopic determination. Fixing only the total energy E of an N-body system leaves the other $(6N-1)$-degrees of freedom unspecified. A second system with the same energy is most likely not in the same microscopic state as the first, it will be at another point in phase space, the other dof's will be different. I.e. the measurement of the total energy $\hat{H}_N$, or any other macroscopic observable $\hat{M}$, determines a $(6N-1)$-dimensional *sub-manifold* $\mathcal{E}$ or $\mathcal{M}$ in phase space. (The manifold $\mathcal{M}$ is called by Lebowitz a *macro-state* [19, 11] which contains

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[¶]The curly brackets indicate the whole set of $6N$ coordinates q_i, p_i of all particles i

$\Gamma_M = W(M)$ micro-states. I, however, prefer to use the name "state" only for micro-states or points in phase space.) All points (the micro-states) in N-body phase space consistent with the given value of E and volume V, i.e. all points in the $(6N-1)$-dimensional sub-manifold $\mathcal{E}(N,V)$ of phase space are equally consistent with this measurement. $\mathcal{E}(N,V)$ is the micro-canonical ensemble. This example tells us that *any macroscopic measurement is incomplete and defines a sub-manifold of points in phase space not a single point.* An additional measurement of another macroscopic quantity $\hat{B}\{q,p\}$ reduces $\mathcal{E}$ further to the cross-section $\mathcal{E} \cap \mathcal{B}$, a $(6N-2)$-dimensional subset of points in $\mathcal{E}$ with the volume:

$$W(B,E,N,V) = \frac{1}{N!} \int \left(\frac{d^3q \, d^3p}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q,p\}) \, \delta(B - \hat{B}\{q,p\}), \qquad (15)$$

If $\hat{H}_N\{q,p\}$ as well as also $\hat{B}\{q,p\}$ are continuous differentiable functions of their arguments, which I assume in the following, then $\mathcal{E} \cap \mathcal{B}$ is closed. In the following I use W for the Riemann or Liouville volume (Hausdorff measure) of a many-fold.

Micro-canonical thermo*statics* gives the conditional probability $P(B|E,N,V)$ to find the N-body system in the sub-manifold $\mathcal{E}(N,V) \cap \mathcal{B}(N,V)$:

$$P(B|E,N,V) = \frac{W(B,E,N,V)}{W(E,N,V)} = e^{\ln[W(B,E,N,V)] - S(E,N,V)} \qquad (16)$$

This is what Krylov seems to have had in mind [40] and what I will call the "ensemble probabilistic formulation of Statistical Mechanics (EPS) " [41].

Similarly thermo*dynamics* describes the development in time of some macroscopic observable $\hat{B}\{q_t, p_t\}$ of systems which were specified at an earlier time t_0 by another macroscopic measurement $\hat{A}\{q_0, p_0\}$. It is related to the volume of the sub-manifold $\mathcal{M}(t,t_0) = \mathcal{A}(t_0) \cap \mathcal{B}(t) \cap \mathcal{E}$:

$$W(A,B,E,t) = \frac{1}{N!} \int \left(\frac{d^3q_t \, d^3p_t}{(2\pi\hbar)^3} \right)^N \delta(B - \hat{B}\{q_t, p_t\}) \, \delta(A - \hat{A}\{q_0, p_0\}) \, \epsilon_0 \, \delta(E - \hat{H}\{q_t, p_t\}), \qquad (17)$$

where $\{q_t\{q_0, p_0\}, p_t\{q_0, p_0\}\}$ is the set of trajectories solving the Hamilton-Jacobi equations

$$\dot{q}_i = \frac{\partial \hat{H}}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial \hat{H}}{\partial q_i}, \qquad i = 1 \cdots N \qquad (18)$$

with the initial conditions $\{q(t=t_0) = q_0; \, p(t=t_0) = p_0\}$.

For a large system with $N \sim 10^{23}$ the probability to find a given value $B(t)$, $P[B(t)]$, is usually sharply peaked as function of B at its typical value. Such systems are called self-averaging. Ordinary thermodynamics treats systems in the thermodynamic limit $N \to \infty$ and gives only $<B(t)>$. However, here we are interested to formulate the Second Law for "Small" systems

14

i.e. we are interested in the whole distribution $P[B(t)]$ not only in its mean value $<B(t)>$. There are also many situation where the system is not self-averaging, where a finite variance remains even in the thermodynamic limit. (E.g. at phase transitions of first order the energy *per particle* fluctuates in the canonical ensemble by the specific latent heat.)

There is an important property of macroscopic measurements: Whereas at finite times Hamilton dynamics evolves a compact region of phase space again into a compact region, this does not need to be so at infinite times. Then, at $t \to \infty$, the set may not be closed anymore (perhaps a fractal, see below). This means there exist series of points $\{a_n\} \in \mathcal{A}(t = \infty)$ which converge to a point $\lim_{n \to \infty} a_n =: a_{n=\infty}$ which is *not* in $\mathcal{A}(t = \infty)$. E.g. such points $a_{n=\infty} \notin \mathcal{A}(\infty)$ may have intruded from the phase space complementary to $\mathcal{A}(t_0)$. Illustrative examples for this evolution of an initially compact sub-manifold into a fractal set are the generalized baker transformations discussed in this context by ref. [42, 43]. See reference [44] for the fractal distribution produced by the general baker transformation. (As any housewife knows, a baker dough becomes an infinitely thin (fractal) puff pastry after pounding and folding it infinitely often.) Only with *infinite resolution* this fractal distribution in phase space can be seen. No macroscopic (incomplete) measurement can resolve $a_{n=\infty} \notin \mathcal{A}(t = \infty)$ from its immediate neighbors $a_n \in \mathcal{A}(t = \infty)$ in phase space with distances $|a_n - a_{n=\infty}|$ less then any arbitrary small δ. In other words, *at the time $t \to \infty$ no macroscopic measurement with its incomplete information about $\{q_{t=\infty}, p_{t=\infty}\}$ can decide whether $\{q_0\{q_{t=\infty}, p_{t=\infty}\}, p_0\{q_{t=\infty}, p_{t=\infty}\}\} \in \mathcal{A}(t_0)$ or not.* I.e. any macroscopic theory like thermodynamics can only deal with the *closure* of $\mathcal{A}(t \to \infty)$. (The closure of a set of points $\mathcal{A}$ is defined as the set plus its limiting points $a_{n=\infty}$, also called boundary points [44]). If necessary, the sub-manifold $\mathcal{A}(t \to \infty)$ must be artificially closed $^{\|}$ to $\overline{\mathcal{A}(t = \infty)}$ as developed further in section 4.2. *Clearly, in this approach this is the origin of irreversibility.*

Before going on, we must make a remark about what means infinite times in reality. This is certainly a typical mathematical idealization: There are several "coarse graining" processes due to which the resolution of points in phase-space as demanded above is strongly reduced: First due to quantum mechanics there is an ultimate coarse graining over sizes of $\delta p \times \delta x \sim 2\pi\hbar$. Second, and more important is the strong smearing discussed above due to the highly reduced macroscopic information about the manifold $\mathcal{A}(t)$. This of course, demands some detailed estimate depending on the actual system.

4.2   Fractal distributions in phase space, Second Law

Let us examine the following Gedanken experiment: Suppose the probability to find our system at points $\{q_t, p_t\}_1^N$ in phase space is uniformly distributed for times $t < t_0$ over the sub-manifold $\mathcal{E}(N, V_1)$ of the N-body phase space at energy E and spatial volume V_1. At time $t > t_0$ we

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$^{\|}$First $t \to \infty$ then the closure, not the other way round c.f. however, the discussion in the conclusion 5.

allow the system to spread over the larger volume $V_2 > V_1$ without changing its energy. If the system is *dynamically mixing*, the majority of trajectories $\{q_t, p_t\}_1^N$ in phase space starting from points $\{q_0, p_0\}_1^N$ with $q_0 \in V_1$ at t_0 will now spread over the larger volume V_2. As already argued by Gibbs [5, 6] the distribution $\mathcal{M}(t, t_0)$ will be filamented like ink in water and will approach any point of $\mathcal{E}(N, V_2)$ arbitrarily close. $\lim_{t \to \infty} \mathcal{M}(t, t_0)$ becomes dense in the new, larger $\mathcal{E}(N, V_2)$. (That is what "mixing" means [45].) The *closure* $\overline{\mathcal{M}(t = \infty, t_0)}$ becomes equal to $\mathcal{E}(N, V_2)$. This is clearly expressed by Lebowitz [11, 19]. Of course the Liouvillean measure of the distribution $\mathcal{M}(t, t_0)$ in phase space at $t > t_0$ will remain the same ($= tr[\mathcal{E}(N, V_1)]$) [46]:

$$
\begin{aligned}
tr[\mathcal{M}(t, t_0)]|_{\{q_0 \in V_1\}} &= \int_{\{q_0\{q_t, p_t\} \in V_1\}} \frac{1}{N!} \left(\frac{d^3 q_t \, d^3 p_t}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_t, p_t\}) \\
&= \int_{\{q_0 \in V_1\}} \frac{1}{N!} \left(\frac{d^3 q_0 \, d^3 p_0}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_0, p_0\}), \quad (19)
\end{aligned}
$$

$$
\text{because of: } \frac{\partial\{q_t, p_t\}}{\partial\{q_0, p_0\}} = 1, \quad (20)
$$

(The label $\{q_0 \in V_1\}$ of the integral means that the positions $\{q_0\}_1^N$ are restricted to the volume V_1, whereas the momenta $\{p_0\}_1^N$ are unrestricted.)

In order to express this fact mathematically, I transform integrals over the phase space like (15) by changing to a new set of orthogonal variables:

$$
W(E, N, t, t_0) = \frac{1}{N!} \int_{\{q_0\{q_t, p_t\} \subset V_1\}} \left(\frac{d^3 q_t \, d^3 p_t}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_t, p_t\}) \quad (21)
$$

into:

$$
\int \left(d^3 q_t \, d^3 p_t \right)^N \cdots = \int d\sigma_1 \cdots d\sigma_{6N} \cdots \quad (22)
$$

$$
d\sigma_{6N} := \frac{1}{||\nabla \hat{H}||} \sum_i \left(\frac{\partial \hat{H}}{\partial q_i} dq_i + \frac{\partial \hat{H}}{\partial p_i} dp_i \right) = \frac{1}{||\nabla \hat{H}||} dE \quad (23)
$$

$$
||\nabla \hat{H}|| = \sqrt{\sum_i \left(\frac{\partial \hat{H}}{\partial q_i} \right)^2 + \sum_i \left(\frac{\partial \hat{H}}{\partial p_i} \right)^2} \quad (24)
$$

$$
W(E, N, t, t_0) = \frac{1}{N!(2\pi\hbar)^{3N}} \int_{\{q_0\{q_t, p_t\} \subset V_1\}} d\sigma_1 \cdots d\sigma_{6N-1} \frac{\epsilon_0}{||\nabla \hat{H}||}. \quad (25)
$$

Now, I *redefine* Boltzmann's definition of entropy eq.(1 to 3): by replacing the Riemannian integral for W by its *box-counting* "measure":

$$
W(E, N, V) \to \not{B}_d \int_{\{q_0\{q_t, p_t\} \in V_1\}} d\sigma_1 \cdots d\sigma_{6N-1} \frac{\epsilon_0}{N!(2\pi\hbar)^{3N}||\nabla \hat{H}||}, \quad (26)
$$

16

i.e. the volume of $\mathcal{M}$ by that of its closure $\overline{\mathcal{M}}$. In detail we perform the following steps:

$$M_\delta(t, t_0) :=<G>_\delta *\mathrm{vol}_{box,\delta}[\mathcal{M}(t, t_0)], \tag{27}$$

to obtain $\mathrm{vol}_{box,\delta}[\mathcal{M}(t, t_0)]$ we cover the d-dim. sub-manifold $\mathcal{M}(t, t_0)$, here with $d = (6N - 1)$, of the phase space by a grid with spacing δ and count the number $N_\delta \propto \delta^{-d}$ of boxes of size δ^{6N}, which contain points of $\mathcal{M}(t, t_0)$. [The following example may explain this: To measure the area A of a sheet of paper in 3d-space one may cover the 3d-space by a grid of 3d-boxes of size δ^3. Only about $N_\delta = A\delta^{-2}$ boxes cut the paper. The area of the paper is then $A = \lim_{\delta \to 0} \delta^2 \times N_\delta$.] This is illustrated by fig.(3). Then $\mathrm{vol}_{box,\delta}[\mathcal{M}(t, t_0)] := \delta^d N_\delta[\mathcal{M}(t, t_0)]$ and $< G >_\delta$ is the average of $\frac{\epsilon_0}{N!(2\pi\hbar)^{3N}||\nabla\hat{H}||}$ over these non-empty boxes of size δ. The $\underline{\lim}_{\delta \to 0}\mathrm{vol}_{box,\delta}[\mathcal{M}(t, t_0)]$ is the box-counting volume of $\mathcal{M}(t, t_0)$ which is the same as the volume of its closure $\overline{\mathcal{M}(t, t_0)}$, see below:

$$\begin{aligned} \mathrm{vol}_{box}[\mathcal{M}(t, t_0)] &:= \underline{\lim}_{\delta \to 0}\delta^d N_\delta[\mathcal{M}(t, t_0)] \tag{28}\\ \text{with } \underline{\lim} * &= \inf[\lim *] \text{ and write symbolically:}\\ \lim_{\delta \to 0} M_\delta(t, t_0) &= \lim_{\delta \to 0} <G>_\delta *\mathrm{vol}_{box,\delta}[\mathcal{M}(t, t_0)]\\ &=: \oiint_d {}_{\{q_0\{q_t,p_t\}\in V_1\}} \frac{1}{N!}\left(\frac{d^3q_t\, d^3p_t}{(2\pi\hbar)^3}\right)^N \epsilon_0\delta(E - \hat{H}_N), \tag{29} \end{aligned}$$

where $\oiint_d$ means that this integral should be evaluated via the box-counting volume (the limit of expression (27) with the use of (28) here with $d = 6N - 1$. This is illustrated by Fig.(3).

The volume of phase space covered by $M_\delta(t, t_0)$ is $\geq W(E, N, V_1)$. Because the manifold remains compact for finite times and because of Liouville's theorem eq.(20), see also section (4.1), we have

$$\underline{\lim}_{\delta \to 0}M_\delta(t, t_0) = W(E, N, t_0, t_0) = W(E, N, V_1) \tag{30}$$

At $t \to \infty$ the two limits $\delta \to 0, t \to \infty$ do in general not commute and as assumed by Gibbs, in the case of a mixing dynamics, the manifold $\mathcal{M}(t \to \infty)$ becomes dense in the new micro-canonical manifold $\mathcal{E}(V_2)$. Then

$$\underline{\lim}_{\delta \to 0} \lim_{t \to \infty} M_\delta(t, t_0) = W(E, N, V_2) > W(E, N, V_1). \tag{31}$$

This is the Second Law of Thermodynamics.
The box-counting is also used in the definition of the Kolmogorov entropy, the average rate of entropy gain [44, 47]. The box-counting "measure" is analogous to the standard method to determine the fractal dimension of a set of points [47] by the box-counting *dimension*:

$$\dim_{box}[\mathcal{M}(t, t_0)] := \underline{\lim}_{\delta \to 0}\frac{\ln N_\delta[\mathcal{M}(t, t_0)]}{-\ln \delta}. \tag{32}$$
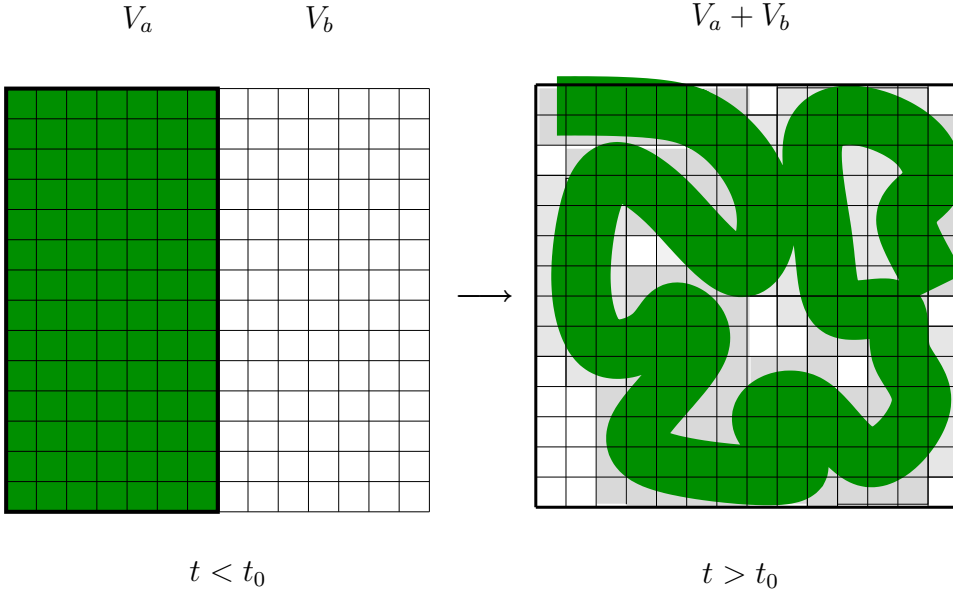
17

Figure 3: The compact set $\mathcal{M}(t_0)$, left side, develops into an increasingly folded "spaghetti"-like distribution $\mathcal{M}(t, t_0)$ in the phase-space with rising time t. The right figure shows only the early form of the distribution. At much later times it will become more and more fractal and finally dense in the new phase space. The grid illustrates the boxes of the box-counting method. All boxes which overlap with $\mathcal{M}(t, t_0)$ contribute to the box-counting volume $\mathrm{vol}_{box,\delta}$ and are shaded gray. Their number is N_δ

Like the box-counting dimension, the box-counting "measure" has the peculiarity that it is equal to the measure of the smallest *closed* covering set. E.g.: The box-counting volume of the set $\mathbf{Q}$ of rational numbers between 0 and 1 is $\mathrm{vol}_{box}\{\mathbf{Q}\} = 1$, and thus equal to the measure of the *real* numbers, c.f. Falconer [47] section 3.1. This is the reason why the box-counting "measure" is not a measure in its mathematical definition because then we should have

$$\mathrm{vol}_{box}\left[\sum_{i\in\{\mathbf{Q}\}}(\mathcal{M}_i)\right] = \sum_{i\in\{\mathbf{Q}\}}\mathrm{vol}_{box}[\mathcal{M}_i] = 0, \tag{33}$$

therefore the quotation marks for the box-counting "measure", c.f. appendix 7.

Coming back to the the end of section (4.1), the volume $W(A, B, \cdots, t)$ of the relevant ensemble, the *closure* $\overline{\mathcal{M}(t, t_0)}$ must be "measured" by something like the box-counting "measure" (26) with the box-counting integral $\displaystyle\oint_{d\delta}$ which must replace the integral in eq.(3). Because the box-counting volume is equal to the volume of the smallest *closed* covering set, the new, extended, definition of the phase-space integral eq.(26) is for compact sets like the equilibrium distribution $\mathcal{E}$ identical to the old one eq.(3) and our redefinition of the phase-space integral by

18

box-counting changes nothing for equilibrium statistics. *Therefore, one can simply replace the old (Riemannian) Boltzmann-definition of the number of complexions (i.e. micro-states) and with it of the entropy by the new one (26) of course with the understanding that the closure operation should be done* after *the times were specified.* In this context it is interesting to notice that Boltzmann was originally thinking of the phase-space discretized into small but finite cells (!), see Gallavotti, page 41 [37].

5 Conclusion

The great conceptual clarity of micro-canonical thermo-statistics compared to the grand-canonical one is again clearly demonstrated. This is due to the strict derivation of thermo-statistics from the basic principles of mechanics, an old dream of Boltzmann. Essential for this goal is the avoidance of the thermodynamic limit. Only then phase transitions as the most interesting phenomena of thermodynamics reveal their underlying physics, the creation of inhomogeneities and interfaces. A further benefit of doing so is that the extended theory applies to a much greater world: the non-extensive or "Small" sytems.

In this paper I showed that Boltzmann's principle eq.(1) covers in a simple and straight way both of Lebowitz's central issues of statistical mechanics [11]: The *appearance of phase transitions* and the *geometrical origin of the Second Law.* Earlier formulations of these ideas can be found in [48, 49]. Lebowitz emphasizes the necessity of self-averaging for thermodynamics which describes the *typical* outcome of a macroscopic measurement. This can only be expected for large systems, in the thermodynamic limit. However, *there are many situations where even large systems are not self-averaging.* E.g. at phase transitions of first order. Moreover, a whole world of non-extensive systems, like the "Small" systems, show broad, often not single peaked, phase-space distributions. An *extension* of statistical mechanics to cover also these is demanded.

Macroscopic measurements $\hat{M}$ determine only a very few of all $6N$ *dof*'s. Any macroscopic theory like thermodynamics deals with the *area* W of the corresponding closed sub-manifold $\overline{\mathcal{E}}$ in the $6N$-dim. phase space not with single points. *Thermodynamics describes the behavior of averages over this manifold.* The explicit averaging over ensembles, or finite sub-manifolds in phase space, becomes especially important for the micro-canonical ensemble of a *finite* or any other non-self-averaging system. E.g. in scattering experiments on nuclei or atomic clusters an average over millions of events is taken. Thus the whole distribution in the accessible phase space is explored. In numerical simulations of phase transitions in finite systems this is done by Monte Carlo averaging over the distribution in phase space.

Because of this necessarily coarsen information, macroscopic measurements, and with it also macroscopic theories are unable to distinguish fractal sets $\mathcal{M}$ from their closures $\overline{\mathcal{M}}$. Therefore, I make the conjecture: the proper manifolds determined by a macroscopic theory like

thermodynamics are the closed $\overline{\mathcal{M}}$. However, an initially closed subset of points at time t_0 does not necessarily evolve again into a closed subset at $t = \infty$ *and the closure operation must be explicitly done after setting the times in order to obtain a quantity that is relevant for a macroscopic theory and can be compared to thermodynamics.* As the closure operation and the $t \rightarrow \infty$ limit do not commute, the macroscopic dynamics becomes irreversible.

Here is the origin of the misunderstanding by the famous reversibility paradoxes which were invented by Loschmidt [50] and Zermelo [38, 39] and which bothered Boltzmann so much [51, 52]. These paradoxes address to trajectories of *single points* in the N-body phase space which must return after Poincaré's recurrence time or which must run backwards if all momenta are exactly reversed. Therefore, Loschmidt and Zermelo concluded that the entropy should decrease as well as it was increasing before. The specification of a single point in $6N$-dim phase-space and the reversion of all its $3N$ momentum components demands of course a *microscopic exact* specification of all $6N$ degrees of freedom not a determination of a few macroscopic degrees of freedom only. As becomes clear from what was said above: *No entropy is defined for a single point. This applies also to the derived thermodynamic quantities like temperature $T = [\partial S / \partial E]^{-1}$ or pressure $P = \frac{\partial S / \partial V}{\partial S / \partial E}$.* Thermodynamics is addressed to the whole manifold, ensemble of systems, with the same macroscopic constraints. The ensemble develops irreversibly even though the underlying Newtonian dynamics of each phase-space point is fully reversible. It is highly unlikely that *all* points in the ensemble $\mathcal{M}(t, t_0)$ have commensurable recurrence times so that they can return *simultaneously* to their initial positions. *Once the manifold has spread over the larger phase space it will never return.*

Also other misinterpretation of Statistical Mechanics are pointed out: The existence of phase transitions and critical phenomena are *not* linked to the thermodynamic limit. They exist clearly and sharply in "Small", non-extensive systems as well. As is demonstrated by figure (2), the micro-canonical phase diagram shows much more details of the relevant phenomena of various phase transitions than was possible up to now in the conventional canonical approach. Boltzmann's principle describes the equilibrium and the approach towards the equilibrium of extensive as well of non-extensive Hamiltonian systems. By our derivation of micro-canonical Statistical Mechanics for finite, eventually "Small" systems, various non-trivial limiting processes are avoided. Neither does one invoke the thermodynamic limit of a homogeneous system with infinitely many particles nor does one rely on the ergodic hypothesis of the equivalence of (very long) time averages and ensemble averages. As Bricmont [36] remarked Boltzmann's principle is the most conservative way to Thermodynamics but more than that it is the most straight one also. *The single axiomatic assumption of Boltzmann's principle, which has a simple geometric interpretation, leads to the full spectrum of equilibrium thermodynamics including all kinds of phase transitions and including the Second Law of Thermodynamics.*

I take the fact serious that Thermodynamics as well as any other *macroscopic* theory handles ensembles or sub-manyfolds and *not* single points in phase-space. Thus the use of ensemble averages is justified directly by the very nature of macroscopic (incomplete) measurements. En-

tropy $s(e, n)$ is the natural measure of the geometric size of the ensemble. With the Boltzmann definition of $s(e, n)$, Statistical Mechanics becomes a *geometric* theory. The topology of its curvature indicates all phenomena of phase transitions independently of whether the system is "Small" or large. Coarse-graining appears as natural consequence of the ensemble-nature. The box-counting method mirrors the averaging over the overwhelming number of non-determined degrees of freedom. Of course, a fully consistent theory must use this averaging explicitly. Presumably, the rise of the entropy can then already be seen at finite times when the fractality of the distribution in phase space is not yet fully developed. Then one would not depend on the order of the limits $\lim_{\delta \to 0} \lim_{t \to \infty}$ as it was assumed here. The coarse-graining is no more a mathematical ad hoc assumption. It is the necessary consequence of the averaging over the $6N - M$ uncontrolled degrees of freedom. Moreover the Second Law in the EPS-formulation of Statistical Mechanics is not linked to the thermodynamic limit as was thought up to now [11, 19].

In this paper I did not contribute anything to the problem of describing irreversible thermodynamics of stationary dissipative systems as it is discussed e.g. by Gilbert and Dorfman [53, 43], Rondoni and Cohen [54]. As mentioned already, dissipation does not exist in the microscopic dynamics. It is not clear to me how far the inclusion of dissipation predefines the arrow of time already which should have been deduced from the theory. The main problem for me was the derivation of irreversibility from fully time reversible microscopic dynamics under maximally clear conditions, i.e. of a micro-canonical closed, finite system. Gaspard [55, 56] considers systems obeying a dynamics that preserves the phase-space volume, i.e satisfying Liouville's theorem, but under non-equilibrium steady state conditions. Similarly to the present approach he had to coarse grain (width δ) the accessible phase space. In conformity to the standard view of thermodynamics being based on the thermodynamic limit [19] he then proves the rise of the entropy *after the limits* (in that order): first $V \to \infty$, then $\delta \to 0$. However, in this limit also the Poincaré recurrence time becomes infinite and Zermelo's piercing argument becomes blunted. So in this approach Gaspard cannot treat our problem of the Second Law in a *finite closed* Hamiltonian system which seems to me to be the heart of the reversibility paradox.

6 Acknowledgment

7 Appendix

In the mathematical theory of fractals [47] one usually uses the Hausdorff measure or the Hausdorff dimension of the fractal [44]. This, however, would be wrong in Statistical Mechanics. Here I want to point out the difference between the box-counting "measure" and the proper Hausdorff measure of a manifold of points in phase space. Without going into too much mathematical detail I can make this clear again with the same example as above eq.(33): The Hausdorff measure of the rational numbers $\in [0,1]$ is 0, whereas the Hausdorff measure of the real numbers $\in [0,1]$ is 1. Therefore, the Hausdorff measure of a set is a proper measure. The Hausdorff measure of the fractal distribution in phase space $\mathcal{M}(t \to \infty, t_0)$ is the same as that of $\mathcal{M}(t_0)$, $W(E, N, V_1)$. Measured by the Hausdorff measure the phase space volume of the fractal distribution $\mathcal{M}(t \to \infty, t_0)$ is conserved and Liouville's theorem applies. This would demand that thermodynamics could distinguish between any point inside the fractal from any point outside of it independently how close it is. This, however, is impossible for any macroscopic theory or experiment which has only macroscopic information where all unobserved degrees of freedom are averaged over. That is the deep reason why the box-counting "measure" must be taken and is a further origin for irreversibility.

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